

Chemical fingerprinting of gold using laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS)

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Internationally, ~2500 t of gold is produced annually in mining operations covering over 60 countries. South Africa produces ~290 t, Australia and the USA ~260 t each and China ~220 t. Quite naturally very few accurate figures for gold theft internationally are available. However, South African sources estimate that some 35 t of gold were stolen annually from mines and refineries during the period 1994–1998, an amount representing over \$1.5 billion per annum. Because gold is essentially untraceable, it is considered the ideal illicit international currency. The requirement to identify the source of stolen gold has resulted in the development of a gold fingerprinting protocol, using laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS), the use of which has significantly increased over the last 20 years. This paper overviews the development and application of the technology and highlights its use in specific cases of gold theft.

KEYWORDS: chemical fingerprinting, gold theft, LA-ICP-MS.

INTRODUCTION AND BACKGROUND TO THE ILLICIT TRADE IN GOLD

Gold has always held a fascination for mankind; it is one of the very few coloured metals that occur naturally, another being copper, which was the basis of the Bronze Age culture of the Western World. Gold is often considered the ultimate indication of an individual's wealth and over the centuries has been traded and stolen and more recently used as 'ghost currency' in the illicit international trade in both weapons and drugs. Today, with almost all of the world's alluvial deposits either discovered or worked out, it is necessary to mine gold from host rocks that can contain as little as one part per million of the metal, in initiatives from openpits to deep underground workings. Pre-concentration and preliminary refining of the metal on site, often in remote areas, increases the possibility of illicit removal and trade in the metal and today it is estimated that considerably in excess of \$US2 billion is stolen annually at source from the world's mines and refineries making gold a significant source of income for major crime syndicates. Gold production, annually lost to theft in such countries as South Africa (Coetzee & Horn 2007), makes up for a large percentage of the total production value (Gastrow 2001). The domino effect of job loss leading to a variety of economical and social problems (impoverishment is one of the largest causes of the high crime rate in South Africa) has crippling effects on entire communities in South Africa and compounding the urgency to develop protocols to identify, recover and ultimately stop theft and illicit trade in the metal.

The illegal trade in stolen precious metals is extremely profitable due to their high values and established identities as global currencies. The ultimate beneficiaries of this illegal trade are normally well-organised bodies that are also involved in a variety of other illegal activities, such as drugs and firearms smuggling. These

organisations present a global threat, and should be monitored and opposed on an international level. Established money-laundering systems using gold have been found in many European countries, such as Switzerland and Italy, and from there across the world, including the USA, and South and Central America (Reuter & Truman 2004; Masciandaro 2004; Zdanowicz 2004; Woolner 1994; Baere & Schneider 1990; Lilley 2003; Grosse 2001).

Reportedly, Uruguay became the leading gold supplier to the USA during 1989 even though the country had no gold industry (Williams 1997; Zeldin 1997; Millard 1999). The gold 'trade' was simply a front for laundering profits made in the illegal narcotics trade (Levi & Reuter 2006). International terrorist groups also regularly use gold as a bargaining tool. Prior to and during the US attack on Afghanistan, Al-Qaeda moved large funds out of the country by smuggling gold, diamonds and other precious stones across the borders, and then to Dubai from where the funds were spread across the world, including the USA (Shehu 1997; El Qorchi *et al.* 2003; Warde 2007). Due to the general absence of formal banking systems in the Middle East, North Africa and Asia the informal Hawala system is often used to refund gold deliveries, where money is transferred across large distances by email or telephone calls, and all records destroyed afterward (Abuza 2003; de Goede 2003; Jamwal 2002). These and many other routes exist whereby illegal funds can be legitimised, using precious metals and precious stones, often themselves having been obtained by illegal means.

It is the involvement of organised crime syndicates that makes policing the theft of gold extremely difficult as informants, willing to risk their own and their family's lives, are hard to find. Consequently it is necessary to establish a mechanism that can be used to trace recovered gold back to its source and direct scarce police and security activity specifically to that source. While increasing security at all mine sites to detect and stop theft may not

be a commercially sensible measure, if it is possible to retrospectively establish the provenance of recovered gold it is then possible to target specific mine sites and introduce more rigorous control and monitoring of mine personnel to ultimately reduce the theft of the metal.

Trace-element fingerprinting of gold-containing materials is a technique aimed at the determination and quantification of minor and trace components. The technique allows the unique characterisation of materials as they pass from ores and precious-metal minerals to flotation concentrates, smelter products, and variously refined products. The use of specially designed statistical software allows allocation of individual analyses to material groups and performs a comparison and allocation of probabilities for the similarity to other data in the database (Watling *et al.* 1993).

In geology, understanding the compositional fingerprints should permit the identification of genetic processes, based on the assumption that differences or changes in the ore-forming processes (e.g. intrinsic conditions of hydrothermal fluids or magmas) will be reflected in the trace-element pattern of ore minerals (or of associated minerals which inevitably are also introduced into the beneficiation process). In forensic science, identifying the original source of precious-metal materials recovered during police operations is of huge financial interest. Although crime statistics are incomplete (it is estimated that only 1.4–2.8% of all stolen gold is recovered), indications are that between 0.8 and 1.6% of the world gold production gets stolen annually in South Africa alone (\$250–500 million) with an additional \$20–50 million stolen in Australia (Coetzee & Horn 2011; Walker 1997; Walker & Unger 2009).

Initial research to identify a method for gold-provenance establishment led to the development of the technique of gold spectral-fingerprinting (Watling *et al.* 1993). This technique is based on the premise that gold, associated with a specific mineralising event (an event in geological time, sometimes lasting many millions of years) or extractive process, will inherit a trace-/ultra-trace-element signature unique to that event or process. Native gold is a mineral composed mainly of Au, Ag and Cu in solid solution and contains trace metals as lattice impurities, mineral inclusions, at and along grain boundaries or in surface coatings. The combination of Au, Ag and Cu as primary indicators, together with as wide a range of trace and minor analytes as possible, provides an elemental and isotopic fingerprint or profile which can uniquely identify a deposit or source of the gold. The uniqueness of this metal assemblage facilitates provenance establishment of the gold in question. However, the fingerprint of refined gold may be significantly different to that of natural unprocessed gold obtained from the same ore, although certain elements will remain throughout refining procedures, albeit at much reduced levels, thereby enabling comparison back to the original material and from there potentially to the mine of origin.

ANALYTICAL TECHNIQUE

The analytical technique of choice in gold-provenance establishment is laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS). Research

detailed in this paper was primarily undertaken using an Agilent 7500CS High sensitivity ICP-MS and a New Wave UP213 laser ablation system. This technique has been used successfully to identify elemental association patterns (spectral fingerprint) of processed gold, gold ores and jewelry recovered in police operations in Australia, South Africa, Indonesia, New Zealand, England, Japan, America and Scandinavia. By comparison of elemental association patterns it has been possible to relate processed and unrefined gold back to individual refined batches and mines of origin. LA-ICP-MS (Watling *et al.* 1994) has now been used successfully to obtain the inter-element association pattern, ‘fingerprint’ of gold in forensic investigations internationally (Freeman *et al.* 1994; Kogan *et al.* 1994; Watling 1996; Watling *et al.* 1997), for fingerprinting scene of crime evidence (Herbert & Watling 1997; Watling 1999; Watling *et al.* 1995) and as a provenance-sourcing tool (Outridge *et al.* 1998; Sie *et al.* 1996; Taylor *et al.* 1997). Because the analytical detection limits are so low, a large number of inter-element association patterns can be employed to develop unique trace-/ultra-trace-element associations in gold. Commonly, elemental data are obtained for over 50 elements. Consequently, the number of elements that can usefully be employed to provide data to establish the fingerprint is extremely large thus increasing the robustness of the spectral fingerprint as a provenance establishment tool. Each ablation event consumes only a fraction of a microgram of sample and it is usually possible to retain a significant proportion of the sample for subsequent further forensic examination and corroborative analyses. In addition, samples can also be stored in a physical database for reference into the future. This aspect has considerable appeal as, in any forensic investigation, it is preferable to retain some of the original sample for corroborative analysis. However, a significant problem with LA-ICP-MS is that the analytical area is extremely small (between 20 and 100 μm) and that the coupling efficiency of the laser will vary from sample to sample. The effect of a small sample area is that, if the sample is inhomogeneous, analytical data may vary from analytical site to analytical site. To overcome this, multiple analyses (usually at least 10) are performed on each sample to obtain a representative picture of the spectral fingerprint of the gold being analysed. The fact that coupling efficiency cannot be controlled means that, under a lasing regime where there is high coupling efficiency, more sample will be removed to the analytical plasma than under conditions where there is lower coupling efficiency. Under these conditions analytical sensitivity will vary between sample sites but inter-element ratios will not, and this comparison of inter-element relationships is the basis of gold fingerprinting.

An issue that hinders the widespread use of LA-ICP-MS in forensic science is the shortage of appropriate solid certified reference materials and solid standards in general. Without standards quantitative data and method validation are impossible to achieve. In fact quantitative analysis is a serious problem for LA-ICP-MS because although relative measurements are sufficient in many cases, ultimately where data use in court is required, absolute concentration measurements will become more and more necessary. However, the use of relative inter-element association patterns is perfectly acceptable for provenance establishment purposes.

Instrument response optimisation

National Institute of Standards and Technology Standards (NIST) Glasses, SRM610 and SRM612 are used to optimise the instrument operating parameters. In addition, the use of these standards at the beginning and end of a complete analytical protocol allow quantification of changes in mass response with time to be made. This procedure also facilitates inter-comparison and normalisation of data on a day to day basis. The choice of these samples and not gold is governed by the fact that optimisation requires a steady-state signal and no laser ablation standards for gold exist. The fact that glass and gold are dissimilar sample types, and that plasma loading will be different for the two matrices, is not relevant as the interpretational protocol for fingerprinting is based on the inter-element association pattern of samples and not on absolute analyte quantitation. The use of NIST standards has proved to be robust and extremely convenient. Once optimisation has been achieved, it is necessary to analyse a series of in-house matrix standards to provide a cross-reference to previously obtained data. In practice, three fabricated gold blocks, each weighing approximately 50 g, are analysed either every 10 study samples or a minimum of three times during any specific sample batch. These in-house gold standards were prepared by combining residual gold from a number of case studies. The molten gold was quenched in chilled water to ensure minimal analyte segregation. The actual element mixture and concentration are immaterial as the standards are used simply to ensure correspondence of day to day and ultimately, long-term analytical data. These samples have been used for the last 12 years for this purpose and the data therefore provide a continuous ability to cross reference on a year to year basis and even to cross-validate methodology when changing both laser and ICP instrumentation.

Analytical procedure

Prior to analysis all samples are individually ultrasonicated for 5 minutes in a mixture of 50% ethanol and 50% water to remove all adhering debris. Where the

size of the sample is extremely small, this stage may be omitted and simple reference made to the time/intensity graphs of the individual elements made to establish if surface contamination exists. Under these circumstances a significant peak for such analytes as sodium, aluminum and iron will occur immediately after the first laser pulse and the signal will quickly return to a plateau, representing the bulk analyte concentration of the sample, once the surface contamination has been removed. Ignoring this initial peak can be easily achieved when the time/response curves are inspected. The analytical signal can then simply be integrated after this initial peak thus removing the influence of surface contamination in the overall analysis. Where possible, at least five sites on each gold sample are analysed using the continuous data acquisition facility of the ICP-MS software. This facility allows the operator to view time slices of the data and select individual areas for analytical comparison. Selection of appropriate areas is based on relative uniformity of signal during the analytical event and implies that the areas of the gold being sampled are free from inclusions and more appropriately represent the bulk composition of the gold. The selected areas of all scans are then combined and response counts per second calculated for each element isotope for ultimate comparison using conventional statistical approaches. This aspect is particularly important when establishing the spectral fingerprint of gold as this material can contain exsolved inclusions of extremely wide analytical complexity and it is necessary to have knowledge of the mineralogy and heterogeneity of the samples prior to interpretation. Prolonged laser ablation can often penetrate these zones and give rise to variations in the elemental response pattern. Often variations in elemental concentrations occur associated with regrowth episodes during the emplacement of the gold and can be identified by relating the elemental scan response function to specific areas on the sample.

Sample analysis

Samples are usually mounted for analysis on 25 mm diameter, 3–4 mm thick square Perspex blocks (Figure 1)

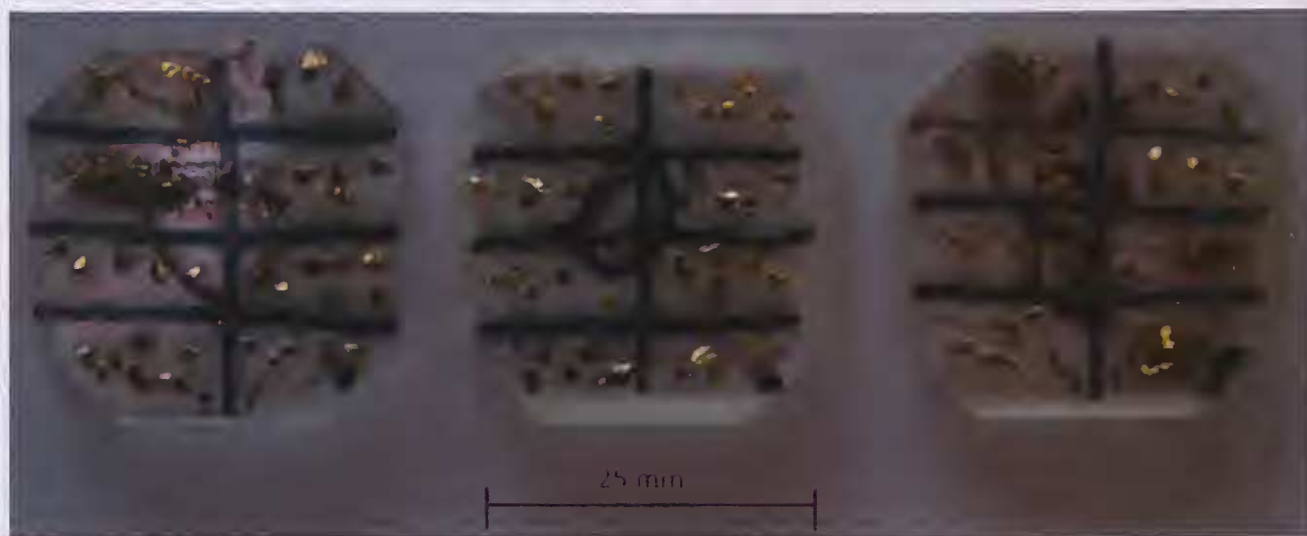
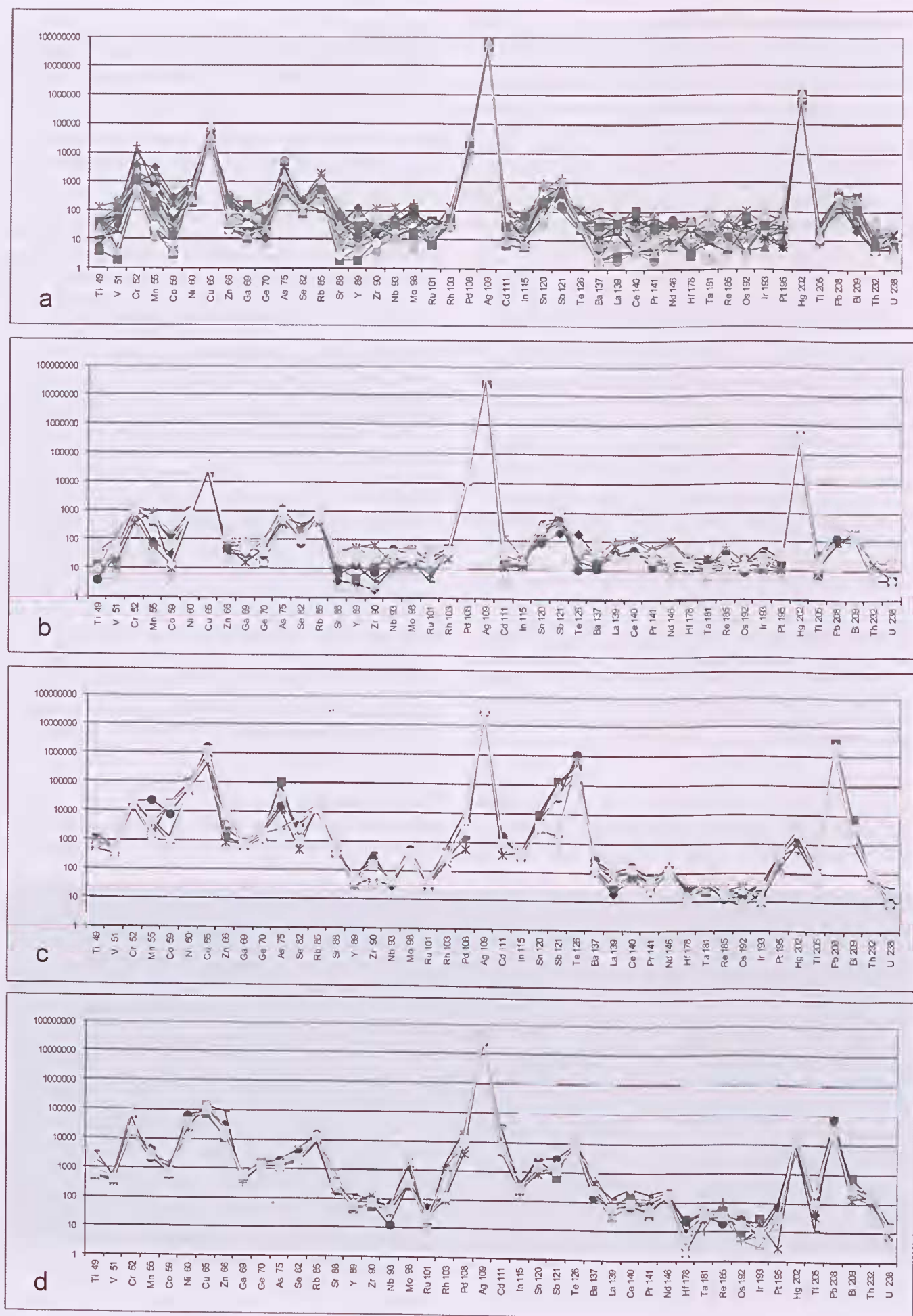


Figure 1 Gold samples mounted for analysis using LA-ICP-MS. (Ideally each block contains at least three replicates of each sample and each block can hold up to eight samples).



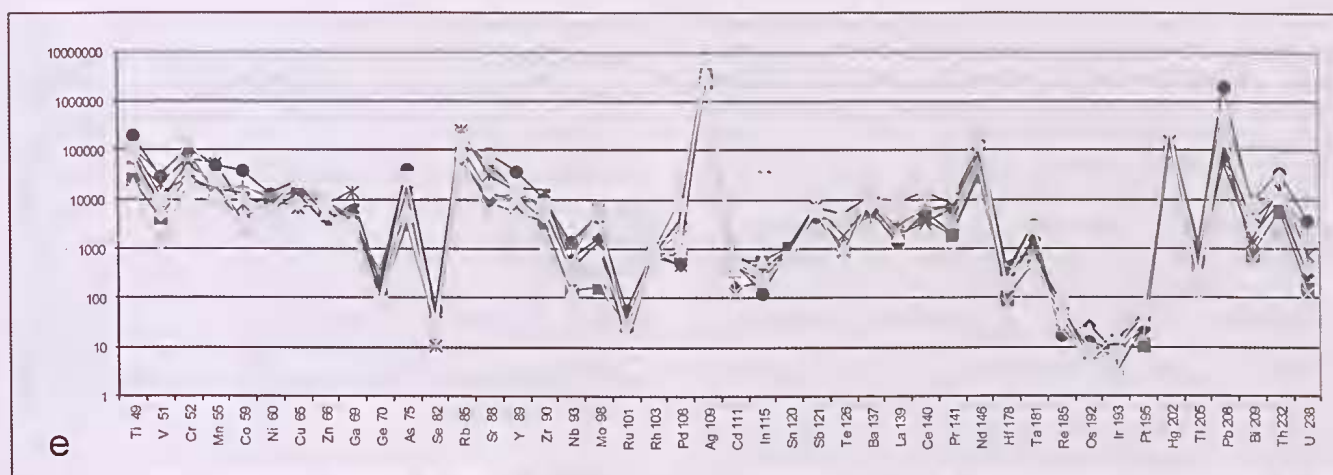


Figure 2 (a) Reproducibility of spectral fingerprint of all samples of stolen gold; (b) of gold from Reference Mine A; (c) of gold from Reference Mine B; (d) of gold from Reference Mine C; (e) of gold from Reference Mine D.

using cyanoacrylate glue as many of the samples received are small (<1 mm³) and even large samples are usually subsampled before analysis. Sample blocks are usually labelled on the back with a reference number (D, E and F in Figure 1) with a blue mark in the upper left hand corner of the upper surface to orient the sample mount under the laser. Samples are then analysed sequentially from the top left to bottom right. A blue colour is used because it is easily identified from any other material on the sample mount.

Ablation is undertaken for ~120 seconds. Data are recorded using a time/response graph where the counts per second data for all analytes are essentially simultaneously recorded with reference to the time post-initiation of lasing. This procedure allows the graph to be inspected retrospectively and when an inclusion of an obviously contaminating ore or gangue mineral has been ablated the analytical data for this time interval is easily apparent and can be retrospectively removed before final counts per second data are computed. The isotopes ⁴⁵Sc, ⁴⁸Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁷¹Ga, ⁷³Ge, ⁷⁵As, ⁸²Se, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ⁹⁸Mo, ¹⁰²Ru, ¹⁰³Rh, ¹⁰⁸Pd, ¹¹¹Cd, ¹¹⁵In, ¹²⁰Sn, ¹²³Sb, ¹²⁶Te, ¹³³Cs, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁵¹Eu, ¹⁵²Sm, ¹⁵⁸Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ¹⁸⁷Re, ¹⁹²Os, ¹⁹³Ir, ¹⁹⁵Pt, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th and ²³⁸U are usually used for gold characterisation. In some cases, however, where an element is present below or close to the detection limit of the technique, it is removed from the data prior to data interpretation.

INTERPRETATION PRINCIPLE

Interpretation of the mass-spectral data, obtained using the protocols described, may be subdivided into the following activities: (i) direct comparison of the raw spectral data; (ii) comparison of the raw count data using comparability statistics; (iii) inter-element association plots; (iv) comparison of data using principal component analysis; and (v) comparison of data using linear discriminant analysis.

Direct comparison of the raw spectral data

Comparison of the inter-element association pattern (fingerprint) is the initial screening test to establish if there are general similarities or differences between the individual spectra under investigation. It could therefore logically be anticipated that inter-element association patterns would be different if gold originated from different mineralising events. Consequently, the confirmation that their fingerprints are different may be considered as a 'proof' of a geologically identifiable observation. The vertical scale on these spectra, which is an approximation of the relative concentration of the abundance of each isotope in the sample, is given on the ordinate. Providing that the spectra are graphically presented on comparable abscissa and ordinate scales, visual comparison is valid to distinguish between both similar and significantly different gold samples. This type of comparison requires significant skill and experience and is often time consuming when a large number of samples have to be compared. Consequently it is useful to sort the spectra into comparable blocks in order to minimise time and assist in the interpretation process.

Comparison of raw count data

Visual comparison of spectral data is frequently demanding with similarities and differences between the actual spectra being difficult to discern and quantify by both trained and untrained personnel. Consequently, comparison of raw count data for selected analytes is often preferred as a simple means of displaying data. This can be achieved extremely quickly using a computerised search/match statistical routine known as a comparability index. The comparability index statistics are based around a sorting subroutine that identifies the logarithmic values of the raw count data and compares these with equivalent element values in the remaining database samples. These differences are then summed and sorted to obtain an approximation of the comparability of the spectra. The series is sorted on the basis of the difference from a 100% fit of the questioned

sample with itself. A 100% fit can only be achieved with absolutely identical spectra being compared, a situation which will never exist in a chemical analysis and is only possible by duplicating the questioned sample in the database. The 100% fit ensures that the maximum possible comparability point is fixed in the interpretational protocol. The worse fit of the questioned sample to one of the other samples in the database is given a 0% comparability rating. Obviously both the top and the bottom database fit are artificial. However, the comparability mathematical routine is only designed to rank the data in the database in order of fit to a questioned sample, and this it does extremely well. Once comparability ranking has been achieved, it is then necessary to visually compare the spectral fingerprint of the high comparability samples to the questioned sample to ensure that the fit is genuine and not an artifact based only on statistics. In addition to simply referring to the numbers (percentage comparability) it is also advisable to plot the percentage comparability relative to the specific sample giving that comparability and its positional number in the database. In this way significant breaks in slope and slope changes in the plot can be observed. These phenomena usually indicate the start of new populations and are a means of sorting data.

Principal component analysis

Principal component analysis (PCA) is a means of assessing the variability of the inter-relationships within a dataset. It is based on the concept of reducing dimensionality in multivariate data and plotting linear combinations of the response variables to explain patterns within the dataset. The defining characteristic of PCA is that its aim is to understand a dataset by considering a group of variables together rather than focusing on only one variable at the time. Fortunately, in datasets with many variables, groups of variables often move together. One reason for this is that more than one variable may be measuring the same driving principle governing the behavior of the system. PCA is a quantitatively rigorous method for achieving an indication of co-association of individual groups of samples. The method generates a new set of variables, called principal components. Each principal component is a linear combination of the original variables. All the principal components are orthogonal to each other so there is no redundant information. The principal components as a whole form an orthogonal basis for the space of the data.

The first principal component is a single axis in space. When each observation is projected on this axis, the resulting values form a new variable. And the variance is the maximum among all possible choices of the first axis. The second principal component is another axis in space, perpendicular to the first. Projecting the observations on this axis generates another new variable. The variance of this variable is the maximum among all possible choices of this second axis. By definition, the full set of the principal components is as large as the original set of variables. But it is commonplace for the sum of the variances of the first few principal components to exceed ~80% of the total variances of the original data. Examination of a few of these new variables can enable the development of a deeper understanding of the driving forces that generated the original data.

Linear discriminant analysis

Discriminant analysis is a method used to model the extent to which an observation belongs to a particular group. The data are described by a series of orthogonal vectors which are possible to graphically represent in a two-dimensional system using two of the determined vectors. The resulting data plot therefore graphically illustrates the presence of groups within the data. Discriminant analysis provides a statistically valid method to test the variation present within the data. This enables the discrimination of gold sources within a sample set. The discriminant analysis was undertaken using the SPSS for Mac statistical software using all analysed isotopes.

RESULTS AND DISCUSSION

In order to better understand the principle of gold spectral fingerprinting it is easier to detail the process by reference to a specific example. In this study, data are presented from an investigation into a possible gold theft where material was thought to have been removed from one or more of four mines in an area of ~400 km². Gold was obtained from each of the mines in question to provide a reference database of samples and the recovered gold compared to results in this database. This investigation highlights the problems associated with gold fingerprinting as variations in the spectral fingerprint will be observed due to inclusions in depth in the gold. Although this aspect increases the complexity of data interpretation the specific fingerprint of the recovered gold is relatively easy to see and significant differences in elemental association patterns within the area can be identified to a level where provenancing is possible. The raw-count data for 44 elements for the stolen and reference gold samples are detailed in Figure 2. A comparability plot (Figure 3) is also detailed to give an indication of relative comparison of all samples in the database. The spectral plots (Figure 2a–e) represent sequentially the relative reproducibility of 39 samples of the recovered stolen gold, 12 samples from the suggested mine of origin (Reference Mine A), 11 samples from Reference Mine B, 12 samples from Reference Mine C and 12 samples from Reference Mine D.

As can be seen from these spectral plots there is an extremely good match between all samples from an individual mine batch. Furthermore, the visual match in the spectral fingerprint of samples shown in Figure 2a and b is excellent while matches between samples of stolen gold shown in Figure 2a with the other three reference mines is extremely poor.

A detailed comparability plot is shown in Figure 3 and the actual comparability percentages detailed in Table 1. Here, simply as an example, a single sample (Recovered gold S17) is matched with the database. The data in the resulting comparability plot (Figure 3) and data table (Table 1) indicate that there is a sliding match of between 99.64% and 97.14% for all recovered gold and all samples from Reference Mine A. At sample Reference Mine C4 (sample 53 in Table 1) there is a significant break in slope in the comparability graph (Figure 3) indicating the start of a completely different series of samples. As indicated previously, this break in slope represents the point where

Table 1 Comparability match for ‘stolen’ gold samples and reference mines.

Sample	Comparability %	Order	Sample	Comparability %	Order	Sample	Comparability %	Order
Rec Gold S17	100	1	Mine A 10	98.45	30	Mine C 6	86.8	59
Rec Gold S17	100	2	Rec Gold S7	98.39	31	Mine B 12	85.8	60
Rec Gold S29	99.6	3	Mine A 12	98.35	32	Mine C 9	85.5	61
Rec Gold S24	99.5	4	Mine A 11	98.29	33	Mine C 7	83.7	62
Rec Gold S1	99.3	5	Rec Gold S22	98.29	34	Mine B 3	82.7	63
Rec Gold S25	99.3	6	Rec Gold S11	98.26	35	Mine C 8	81.7	64
Rec Gold S14	99.3	7	Rec Gold S38	98.16	36	Mine C 10	81.2	65
Rec Gold S33	99.3	8	Rec Gold S12	98.11	37	Mine B 10	80.6	66
Mine A 4	99.2	9	Rec Gold S3	98.11	38	Mine B 9	79.7	67
Mine A 3	99.1	10	Rec Gold S16	98.07	39	Mine B 5	79.6	68
Rec Gold S20	99	11	Rec Gold S18	98.07	40	Mine B 8	79.2	69
Mine A 2	99	12	Rec Gold S32	98.05	41	Mine B 1	78.7	70
Rec Gold S35	98.9	13	Rec Gold S27	97.99	42	Mine B 2	76.5	71
Rec Gold S13	98.9	14	Rec Gold S6	97.98	43	Mine B 7	74.7	72
Rec Gold S5	98.9	15	Mine A 9	97.97	44	Mine B 4	72.6	73
Mine A 1	98.9	16	Rec Gold S28	97.84	45	Mine B 6	71.7	74
Rec Gold S21	98.8	17	Rec Gold S30	97.82	46	Mine B 11	71.4	75
Rec Gold S39	98.8	18	Rec Gold S34	97.8	47	Mine D 12	67.4	76
Mine A 5	98.8	19	Rec Gold S37	97.7	48	Mine D 4	63.2	77
Mine A 8	98.7	20	Rec Gold S15	97.7	49	Mine D 2	54	78
Rec Gold S2	98.7	21	Mine A 7	97.67	50	Mine D 1	47.4	79
Rec Gold S19	98.7	22	Rec Gold S23	97.52	51	Mine D 3	37.7	80
Rec Gold S26	98.7	23	Rec Gold S8	97.14	52	Mine D 10	34.4	81
Rec Gold S4	98.7	24	Mine C 4	89.51	53	Mine D 9	30.6	82
Rec Gold S31	98.7	25	Mine C 5	88.96	54	Mine D 5	22.6	83
Rec Gold S36	98.7	26	Mine C 3	88.11	55	Mine D 11	15.1	84
Rec Gold S9	98.6	27	Mine C 1	87.99	56	Mine D 8	13.9	85
Rec Gold S10	98.6	28	Mine C 11	87.68	57	Mine D 7	13.3	86
Mine A 6	98.6	29	Mine C 2	87.64	58	Mine D 6	0	87

Rec, recovered

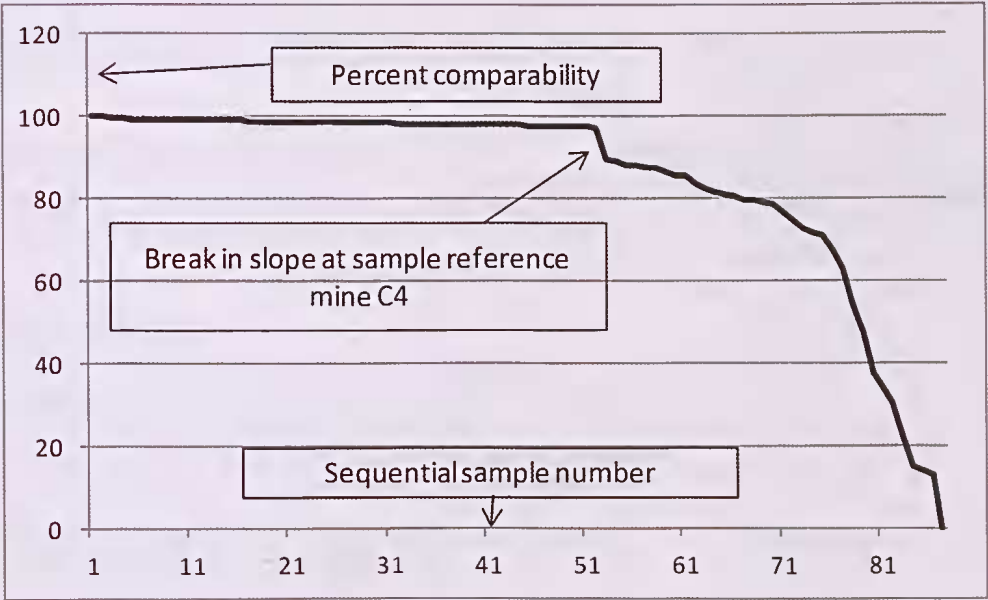


Figure 3 Comparability slope for case samples

it is possible to differentiate between gold from a different source to the reference gold. Consequently it can be inferred from this graph that all samples from Reference Mines B, C and D have a statistically insignificant chance of being co-provenanced with any samples in the so-called batch of stolen gold and represent completely different

mineralising events in the formational processes of the gold ore. When any other sample of gold from either Reference Mine A or stolen gold are compared in the same way an equivalent pattern is generated confirming the observation of co-provenance of samples from Reference Mine A and stolen gold.

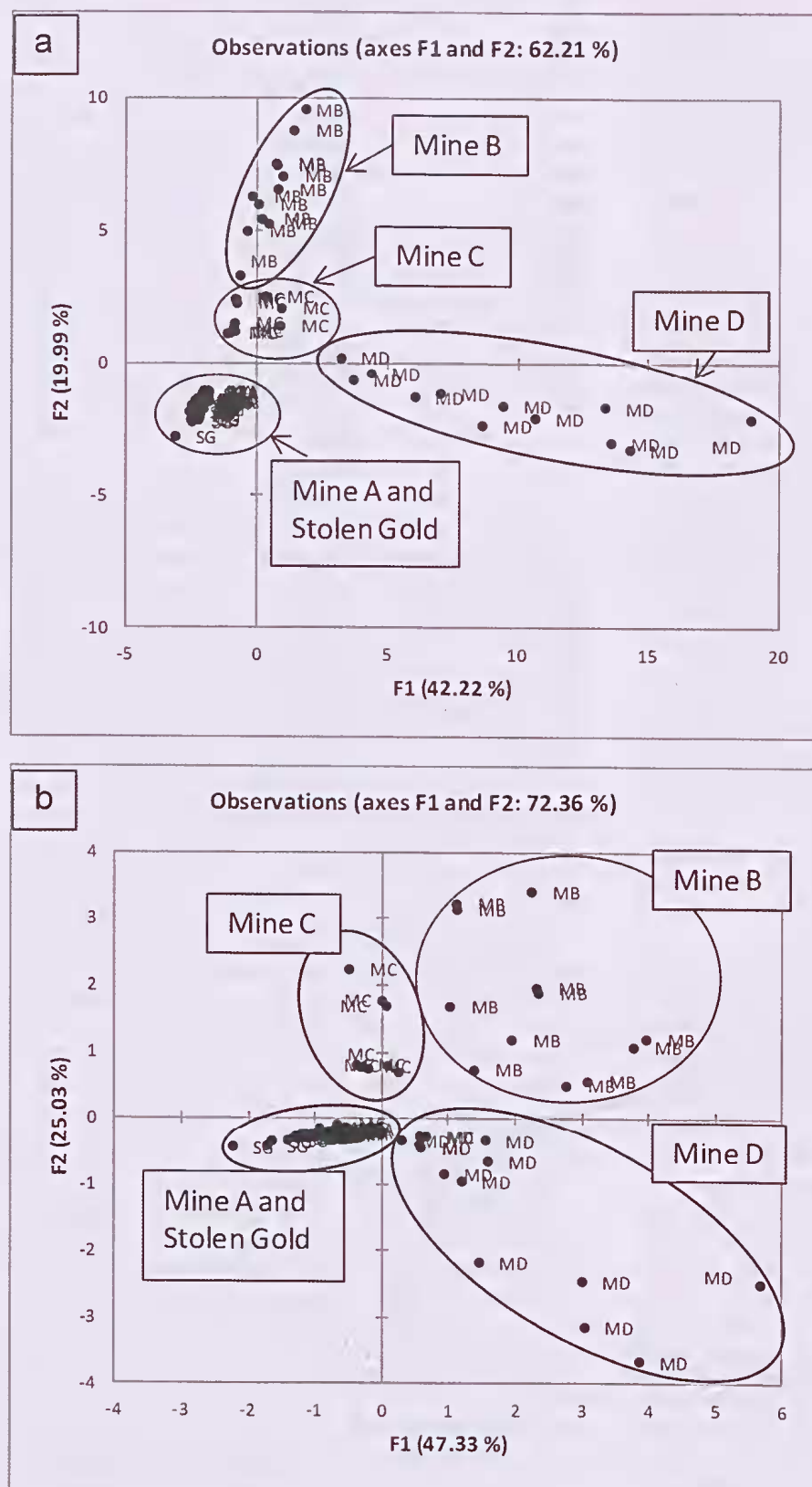


Figure 4 PCA plots for (a) all elements and (b) Pd, Mo, Co, Pb and Se.

Final confirmation of the association of Mine A samples with those of the stolen gold can be achieved by using PCA plots. In this case, it is possible to see by using both the total-element analytical cocktail (Figure 4a) and selected elements (Figure 4b) that the samples of stolen gold group extremely tightly with samples of gold from Mine A and are isolated from samples representing all three other mines. There is some apparent overlap between samples from Mines B and C (Figure 4a) and Mines C and D (Figure 4b). However, isolation of Mines C and D (Figure 4a) and Mines C and B (Figure 4b) allows isolation of these mines from each other and in all interpretational protocols detailed above, it is possible to isolate and unambiguously identify samples from all four mines.

CONCLUSIONS

Laser ablation-ICP-MS provides extremely sensitive analytical data for determining inter-element association patterns for gold samples. While it would be preferred that data were quantitative in nature, it is nonetheless easily possible to use relative raw counts, ternary association diagrams, linear discriminant analysis and principle component analysis to discriminate between the element association patterns of different deposits and thereby identify co-provenance or otherwise of samples. In addition the increase in the number of samples represented in in-house databases is becoming increasingly more important when identifying the generic provenance of samples that are not associated with a specific known mine of origin. When large databases are interrogated it is always possible to associate recovered material with a source, if that source is present on the database. Damage to gold is insignificant and the amount of material removed does not significantly reduce the value of the material. The fact that extremely small samples can be easily analysed also increase the ability to use extremely small samples, often present as microscopic material on floors, carpets and in clothing. Because such a small amount of material is used for analytical purposes, samples can always be provided to either defense or prosecution for corroborative analysis and can also be stored in a spatially very limited physical database for further research and method development.

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